

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of manufacture by micrometre and nanometre scale spatially selective deposition of chemical substances on a substrate, the method including the steps of:
 - (a) defining at least one region on the substrate by forming an electrostatic charge on that region which is different from the electrostatic charge on other regions of the substrate,
 - (b) applying an emulsion to the substrate, the emulsion including an electrically charged discontinuous phase and a component to be selectively deposited carried in or comprising the discontinuous phase, and
 - (c) directing the discontinuous phase of the emulsion to the at least one region by attraction to or repulsion from the electrostatic charge on the region.
2. A method as in Claim 1 wherein the component to be selectively deposited is selected from the group comprising a bio-active agent, an activated nucleoside amidite (A, C, G or T), an activated oligonucleotide, a reagent or reactant including acids and bases, a blocking chemical, a de-blocking chemical, an organic or inorganic derivatisation chemical, a catalyst, a pharmaceutical, a dye or a pigment.
3. A method as in Claim 1 further including the step of carrying out repetition of steps (a) to (c) to provide a stepwise deposition process at the same or alternative positions on the substrate and to achieve combinatorial synthesis on the substrate.
4. A method of manufacture by micrometre and nanometre scale spatially selective deposition of chemical substances on a substrate, the method including the steps of:
 - (a) defining at least one region on the substrate by forming an electrostatic charge on that region which is different from the electrostatic charge on other regions of the substrate,

- (b) applying an emulsion to the substrate, the emulsion having an electrically charged discontinuous phase and a chemical reagent to participate in forming the solid phase array carried in or comprising the discontinuous phase,
- (c) depositing the discontinuous phase of the emulsion to the at least one region
5 by attraction by the electrostatic charge on the region and optionally by the use of bias voltage to reduce deposition in non-required regions,
- (d) causing a chemical or physical reaction in the at least one region, and
- (e) removing the emulsion.

10 5. A method as in Claim 4 further including the step of carrying out repetition of steps (a) to (e) to provide a stepwise deposition process at the same or alternative positions on the substrate.

15 6. A method as in Claim 4 further including the step of flooding with a further reagent wherein reaction of the further reagent only occurs where the spatially selective deposition had previously occurred.

7. A method of forming a solid phase chemical array on a substrate using a stepwise reaction process, the method including the steps of:

- 20 (a) defining at least one region on the substrate by forming an electrostatic charge on that region which is different from the electrostatic charge on other regions of the substrate,
- (b) applying an emulsion to the substrate, the emulsion having the electrically charged discontinuous phase droplets and a chemical reagent carried in or
25 comprising the discontinuous phase,
- (c) depositing the discontinuous phase of the emulsion to the at least one region by attraction by the electrostatic charge on the region and optionally by the use of a bias voltage to reduce deposition in non-required regions,
- (d) causing a chemical reaction in the at least one region,
- 30 (e) removing the emulsion, and
- (f) carrying out subsequent steps of the stepwise reaction process.

8. A method as in Claim 6 wherein the step of applying the emulsion to the substrate includes the step of applying a coating to the substrate of the liquid of the continuous phase or other liquid before applying the emulsion.

5 9. A method of forming a DNA array on the substrate using a stepwise coupling process with a chemical de-protecting step prior to each coupling step, the method including the steps of:

(a) preparing a substrate with surface functional groups protected by a removable protecting group;

10 (b) defining at least one region on the substrate by forming an electric field on that region which is different from the electric field on other regions of the substrate,

(c) applying an emulsion to the substrate, the emulsion having the electrically charged discontinuous phase droplets and a chemical de-protecting reagent carried in the discontinuous phase,

15 (d) depositing the discontinuous phase of the emulsion to the at least one region by attraction by the electric field on the region and optionally by the use of a bias voltage to reduce deposition in non-required regions,

(e) causing chemical de-protecting in the at least one region,

20 (f) removing the emulsion, and

(g) carrying out subsequent steps of the stepwise coupling process.

10. A method as in Claim 9 wherein the subsequent steps of the stepwise coupling process are those in the phosphoramidite chemistry for synthesis of
25 oligodeoxynucleotides.

11. A method as in Claim 9 wherein the continuous phase of the emulsion comprises a liquid which is electrically insulative having a volume resistivity of approximately 1×10^6 ohm-cm or greater.

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12. A method as in Claim 9 wherein the continuous phase of the emulsion is selected from the group comprising hydrocarbons such as hexane, cyclohexane, iso-

octane, decalin, heptane, aromatic hydrocarbons and isodecane and mixtures of hydrocarbons; fluorochemicals including fluorocarbon compounds including linear, cyclic or polycyclic perfluoroalkanes, bis(perfluoroalkyl)alkenes, perfluoroethers, perfluoroalkylamines, perfluoroalkyl bromides and perfluoroalkyl chlorides; silicone
5 fluids such as polyphenylmethyl siloxanes, dimethyl polysiloxanes, polydimethyl siloxanes and cyclic dimethyl siloxanes.

13. A method as in Claim 9 wherein the continuous phase of the emulsion is a gel or highly viscous liquid.

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14. A method as in Claim 9 wherein the discontinuous phase of the emulsion is non-aqueous and is immiscible or substantially insoluble in the continuous phase.

15. A method as in Claim 9 wherein the discontinuous phase of the emulsion is
15 selected from the group comprising a reagent, a solvent which carries an active chemical reagent or a carrier liquid for a solid or insoluble liquid dispersed in the discontinuous phase.

16. A method as in Claim 9 wherein the discontinuous phase of the emulsion is
20 selected from the group comprising acetone, acetonitrile, cyclohexanone, dibromomethane, dichloromethane (methylene chloride, DCM), trichloromethane, dimethyl formamide (DMF), dioxane, 1,2-dichloroethane (DCE), nitromethane, tetrahydrofuran, toluene, decalin, dimethyl formamide, isobutanol, propylene carbonate, dimethyl sulphoxide, commercially available mixtures of hydrocarbons
25 including Isopar™ and Norpar™ or mixtures of compounds such as isopropanol/methylene chloride, nitromethane/methanol, nitromethane/isopropanol, trichloromethane/methanol or isopropanol/methylene chloride.

17. A method as in Claim 9 wherein the emulsion further includes a charge
30 control agent.

18. A method as in Claim 17 wherein the charge control agent is selected from the group comprising an inorganic acid and its salts, an organic acid and its salts or an ionic or zwitterionic compound.

5 19. A method as in Claim 17 wherein the charge control agent is selected from the group comprising metallic soaps, comprising a metal and an acid wherein the metal is selected from barium, calcium, magnesium, strontium, zinc, cadmium, aluminium, gallium, lead, chromium, manganese, iron, nickel, zirconium and cobalt and the acid
10 portion is a carboxylic acid, caproic acid, octanoic (caprylic) acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linolic acid, erucic acid, tallitic acid, resinic acid, naphthenic acid and succinic acid; a phospholipid or alkyl succinimide.

20. A method as in Claim 9 wherein the emulsion comprises the continuous phase
15 present in the range of about 20 to 99.99 per cent by volume, the discontinuous phase present in a range of from about 0.01 to 80 per cent by volume, optionally a surfactant present in a range of about 0.01 to 20 per cent by weight and optionally a charge control agent present in a range of 0.01 to 10 per cent by weight.

20 21. A method as in Claim 9 wherein the emulsion comprises the discontinuous phase has a droplet size of from about 100 microns down to 0.2 microns.

22. A method as in Claim 9 wherein the emulsion is a miniemulsion with a discontinuous phase having a droplet size from 500 nanometres down to about 50
25 nanometres.

23. A method as in Claim 9 wherein the emulsion comprises a microemulsion with a discontinuous phase having a droplet size of from about 200 nanometres down to 1 nanometre.

24. A method as in Claim 9 wherein the step of defining at least one region on the substrate by forming an electrostatic charge on that region includes the step of image reversal to enable deposition in non-charged regions.
- 5 25. A method as in Claim 9 wherein the step of formation of the electrostatic image pattern is by electrostatic means wherein the substrate is a photoconductor and the formation of the electrostatic field is by charging and subsequent discharging by selective illumination.
- 10 26. A method as in Claim 9 wherein the step of removing the emulsion includes the step of neutralising any residual chemical de-capping agent in the emulsion to prevent it from reacting in non-desired parts of the array.
- 15 27. A method as in Claim 9 wherein the chemical deprotection reagent is selected from the group comprising Lewis acids, protic acids, zinc bromide, titanium tetrachloride, and ceric ammonium nitrate, dilute mineral acids, trichloroacetic acid (TCA), dichloroacetic acid (DCA), benzenesulphonic acid, trifluoroacetic acid (TFA), difluoroacetic acid, perchloric acid, orthophosphoric acid, toluenesulphonic acid, dodecylbenzene sulphonic acid and diphenyl acid phosphate.
- 20 28. A method as in Claim 9 wherein the emulsion further includes a surfactant, the surfactant having a first part which is compatible with the continuous phase and a second part which is compatible with the discontinuous phase, the surfactant being selected to not significantly reduce the volume resistivity of the continuous phase.
- 25 29. A method as in Claim 28 wherein the surfactant is selected from the group comprising anionic, cationic, non-ionic or amphoteric compounds, polymer surfactant materials or phospholipids or fluorinated analogues of these.
- 30 30. A method as in Claim 9 wherein the substrate comprises a support, a conductive layer on the support, a dielectric or photoconductive layer of a material which will hold an electric charge and a chemically functional layer.

31. A method as in Claim 30 wherein the support is selected from the group comprising metal, glass, ceramic, or polymeric material
32. A method as in Claim 30 wherein the conductive layer is selected from the group comprising a sputtered layer of metal, indium tin oxide, or salts such as quaternary ammonium salts.
33. A method as in Claim 30 wherein the dielectric or photoconductor layer is selected from the group comprising glass, a polymeric resin such as Mylar (PET, polyethyleneterephthalate), zinc oxide, cadmium sulphide, amorphous selenium, alloys of selenium such as selenium-tellurium, lead selenide, selenium-arsenic and polyvinylcarbazole (PVK).
34. A method of manufacturing a flat screen display of the type having separately illuminable pixels, the method including the steps of;
- i) providing a substrate having a light emitting diode array defining a plurality of pixel sites, each pixel site including an electrode;
 - ii) applying an electric charge to the electrodes of selected pixel sites,
 - iii) providing a liquid composition adapted to apply a colourant, the liquid composition including an insulative liquid and electrically charged colourant of a selected colour;
 - iv) placing the liquid composition onto the substrate;
 - v) attracting the colourant to the selected pixel sites;
 - vi) removing excess liquid composition from the substrate;
 - vii) fixing the colourant to the substrate; and
 - viii) repeating steps ii) to viii) to apply further colourant of other selected colours to other selected pixel sites.
35. A method of manufacturing a flat screen display as in Claim 34 wherein the selected colour includes the colours red, green and blue.

36. A method of manufacturing a flat screen display as in Claim 34 wherein the charge is applied to the selected pixel sites by activating selected ones of the LED array.

5 37. A method of manufacturing a flat screen display as in Claim 34 wherein the light emitting diodes may be organic light emitting diodes.

38. A method of manufacturing a flat screen display as in Claim 34 wherein the insulative liquid is selected from hydrocarbon fluids, silicone fluids, chlorinated
10 hydrocarbons and perfluorocarbons.

39. A method of manufacturing a flat screen display as in Claim 34 wherein the colourant is or is incorporated in charged droplets comprising the discontinuous phase of an emulsion.
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40. A method of manufacturing a flat screen display as in Claim 34 wherein the substrate may be selected from glass, polyester foil, polycarbonate, Mylar™, stainless steel and the like.

20 41. A method of manufacturing a flat screen display as in Claim 34 wherein the substrate includes a coating of indium tin oxide (ITO).

42. A method of manufacturing a flat screen display of the type having separately illuminable pixels,

25 the method including the steps of;

- i) providing a substrate having a conductor array defining a plurality of pixel sites, each pixel site including an electrode;
- ii) applying an electric charge to the electrodes of selected pixel sites,
- iii) providing a liquid composition adapted to apply a selected polymer film to the
30 selected pixel sites, the liquid composition comprising an emulsion including a continuous phase comprising an insulative liquid and a discontinuous phase

comprising electrically charged droplets of or including a polymer to deposit the polymer film;

iv) placing the liquid composition onto the substrate;

v) attracting the droplets to the selected pixel sites;

5 vi) removing excess liquid composition from the substrate;

vii) fixing the polymer to the substrate; and

viii) repeating steps ii) to viii) to apply further selected polymer film to other selected pixel sites.

10 43 A method of manufacturing a flat screen display as in Claim 42 wherein the polymer is a material which exhibits electroluminescence selected from the group comprising poly(phenylene vinylene) (PPV), parylene, polyvinylcarbazole (PVK) and polyfluorene.

15 44. A method of manufacturing a flat screen of display the type having separately illuminable pixels, the method including the steps of;

i) providing a substrate having a conductor array defining a plurality of pixel sites, each pixel site including an electrode;

ii) applying an electric charge to all of the electrodes of the plurality of pixel sites,

20 iii) providing a liquid composition adapted to apply a selected polymer film to the selected pixel sites, the liquid composition comprising an emulsion including a continuous phase comprising an insulative liquid and a discontinuous phase comprising electrically charged droplets of or including a polymer to deposit the polymer film;

25 iv) placing the liquid composition onto the substrate;

v) attracting the charged droplets to the selected pixel sites;

vi) removing excess liquid composition from the substrate;

vii) fixing the polymer to the substrate;

viii) applying an electric charge to selected ones of the electrodes of the plurality of pixel sites,

30 ix) providing a second liquid composition adapted to apply a dye to the selected ones of the pixel sites, the liquid composition comprising an emulsion including a

continuous phase comprising an insulative liquid and a discontinuous phase comprising electrically charged droplets of or including the dye to deposit onto the polymer film;

x) placing the second liquid composition onto the substrate;

5 xi) attracting the charged droplets to the selected pixel sites;

xii) removing excess liquid composition from the substrate;

xiii) fixing the polymer to the substrate; and

xiv) repeating steps viii) to xiii) to apply further selected dye to other selected pixel sites.

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45 A method of manufacturing a flat screen display as in Claim 43 wherein the polymer film fixed to the substrate is a photoconductor and step ix) is achieved by selective illumination of pixel sites.

15 46. A method of manufacturing a flat screen of display the type having separately illuminable pixels, the method including the steps of;

i) defining a plurality of pixel sites on a substrate by generating a electrostatic array pattern on the substrate;

ii) providing a liquid composition adapted to apply a selected polymer film to the

20 defined pixel sites, the liquid composition comprising an emulsion including a continuous phase comprising an insulative liquid and a discontinuous phase comprising electrically charged droplets of or including a polymer to deposit the polymer film;

iii) placing the liquid composition onto the substrate;

25 iv) attracting the droplets to the defined the plurality of pixel sites;

v) removing excess liquid composition from the substrate;

vi) fixing the polymer to the substrate; and

vii) repeating steps i) to vi) to apply further selected polymer film to other defined pixel sites.

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47. A flat screen display panel formed by the method of Claim 34.

48. A flat screen display panel formed by the method of Claim 42.
49. A flat screen display panel formed by the method of Claim 43.
- 5 50. A flat screen display panel formed by the method of Claim 45.
51. A DNA array on a substrate formed by the method of Claim 8.
52. A micrometre and nanometre scale spatially selective deposition of chemical
10 substance on a substrate formed by the method of Claim 1.